SOME SUBSTITUTED STYRENES AND THEIR POLYMERS AND COPOLYMERS WITH BUTADIENE

BY

NUTULAPATY SHANMUKHA RAO

B. Sc., Benares Hindu University, 1942

M. Sc., Benares Hindu University, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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ACKNOWLEDGMENT

The author wishes to express his grateful appreciation to Professor C. S. Marvel for his encouragement and guidance in the prosecution of this investigation. He also wishes to express his thanks to Mrs. A. R. Johnson for the determination of infrared absorption spectra, Dr. N. A. Higgins and Dr. E. R. Alexander for their many helpful suggestions which facilitated this work.

The author is indebted to the Tata Endowment, Bombay, for the scholarship granted for higher education in the United States of America.

This work was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The loss of Malaya during World War II necessitated the development of synthetic rubber for use in all types of vehicle tires. The synthetic rubber produced in large amounts for this purpose, GR-S, is inferior to natural rubber in some properties. A continuous effort has been made to improve the properties of GR-S and to develop new synthetic elastomers which might have properties superior to those of natural rubber.

The major problem involved in the utilization of the butadiene copolymers of styrene is the deficiency of tackiness (1). Considerable time and effort have been expended in trying to improve the tackiness of these copolymers. The tack-producing qualities of a number of the alkyl phenol sulfides were investigated (1). One of the more successful tackifiers a resin known as Koresin was developed by German technologists during World War II; it was prepared by the condensation of *p-tert.*-butylphenol with acetylene in the presence of zinc naphthenate as catalyst (2).

The immediate goal of the present research has been to prepare a polymer differing from GR-S only in that it contains phenolic hydroxyl groups in the chain. An attempt has been made to accomplish this by preparing various hydroxystyrenes or derivatives thereof, copolymerizing these with butadiene, and evaluating the resulting copolymer for tackiness.

Discussion of Results

o-Hydroxystyrene has been prepared from coumarin which

was converted to *trans*-*o*-hydroxycinnamic acid by treating with sodium sulfite and potassium hydroxide according to the procedure of Dodge (3). Decarboxylation of the acid by the method of Fries and Fickewirth (4) yielded o-hydroxystyrene.

o-Acetoxystyrene was made from *o*-hydroxystyrene by acetylation with acetic anhydride in the presence of sodium acetate. The procedure employed for acetylation was that of Borders and Greer (5).

p-Methoxystyrene was synthesized from anisole according to the procedure of Quelet and Ducasse (6). Chloroethylation with paraldehyde and hydrochloric acid gave α-chloroethyl anisole. Dehydrohalogenation by treatment with pyridine resulted in the formation of *p*-methoxystyrene.

A polymer of each of the substituted styrenes was made; *o*-hydroxystyrene and *p*-methoxystyrene were polymerized by exposing to ultraviolet light for thirteen to twenty-two days, and *o*-acetoxystyrene was polymerized by heat. Poly-(*p*-methoxystyrene) could not be successfully demethylated by hydriodic acid. Neither *o*-hydroxystyrene nor *o*-acetoxystyrene would polymerize with butadiene either in the mutual recipe, a redox formula or in acidic emulsion system. Further, *o*-hydroxystyrene failed to copolymerize with butadiene in the presence of a cationic catalyst.

o-Acetoxystyrene copolymerized with butadiene and styrene in a cationic system. Carbon tetrachloride was used as the diluting medium and stannic chloride as the catalyst. The infrared absorption spectrum of the terpolymer obtained showed the existence of acetoxy groups proving thereby that *o*-acetoxystyrene has entered the polymer chain.

Hydroxyl groups were liberated by hydrolysis of the acetoxy groups with aqueous hydrochloric acid. The infrared spectrum of the hydrolysed polymer indicated the presence of phenolic hydroxyl groups. A sample of this polymer—a

GR-S type containing phenolic hydroxyl groups—was submitted for evaluation as a tackifier.

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VITA

The author was born in Perakalapudy, India, on June 1, 1921. He attended the elementary school in Perakalapudy and was matriculated from the Municipal High School, Bezwada, in 1937. He completed the first two years at the Andhra Christian College, Guntur. He joined the Benares Hindu University in 1940 and received the degree of B. Sc. (Industrial Chemistry), securing the highest percentage of marks in June, 1942. He was the recipient of R. B. Mata Prasad Prize; and the University Merit Scholarship for the next two years. In 1944 he received M. Sc. degree in chemistry. From July, 1944, to February, 1945, he worked as a J. K. Fellow in the Chemistry Department at the Benares Hindu University. He was awarded a Tata Scholarship for higher education in the United States of America in February, 1945. He enrolled in the Graduate School at the University of Illinois in October, 1945. Since June, 1946, he has held a Special Research Assistantship in Chemistry on the Rubber Research Program, Rubber Reserve, Reconstruction Finance Corporation.

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